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(71) Applicant:000003078
Kabushikikaisya Toshiba
72 Horikawamachi, Saiwai-ku, Kawasaki-shi,Kanagawa
(72) Inventor:Miho Suzuki
8 shinnsugitamachi,Isogo-ku,Yokohama-shi, Kanagawa
c/o Kabushikikaisya Toshiba, Yokohama Jigyosyo
(72) Inventor: Toshio Ikeda
8 shinnsugitamachi,Isogo-ku,Yokohama-shi, Kanagawa
c/o Kabushikikaisya Toshiba, Yokohama Jigyosyo
(72) Inventor: Norio Takeyama
8 shinnsugitamachi,Isogo-ku,Yokohama-shi, Kanagawa
c/o Kabushikikaisya Toshiba, Yokohama Jigyosyo
(74)Agent:Patent Attorney;Hidekazu Miyoshi(and three others)

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(54) Title of the Invention: A DECOMPOSITION APPARATUS FOR HALOGEN-CONTAINING ORGANIC COMPOUND

(57)[Abstract]

[Object]

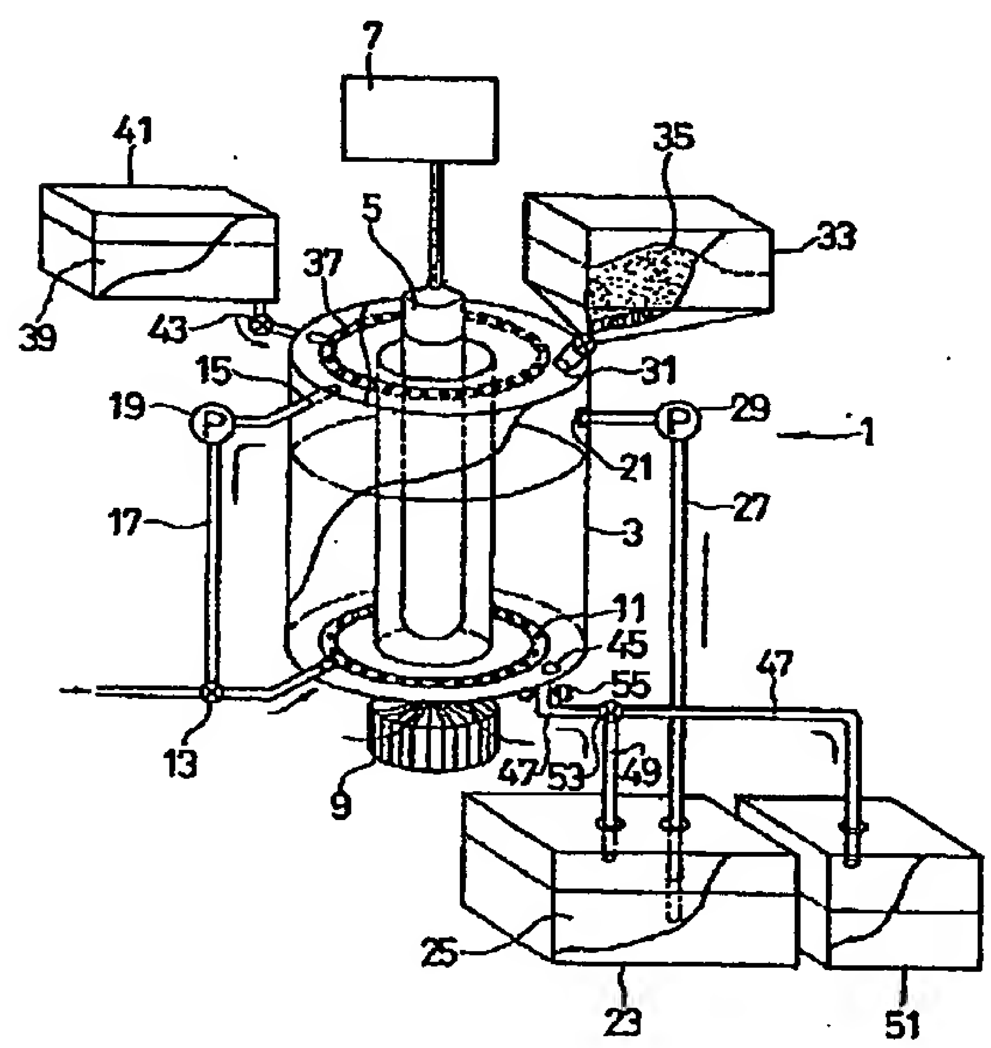
To provide a decomposition apparatus for a halogen-containing organic compound which can achieve downsizing, easy maintenance, and the like.

[Constitution]

A decomposition apparatus for a halogen-containing organic compound of the present invention is a decomposition apparatus for a halogen-containing organic compound for irradiating ultraviolet rays and thereby decomposing a halogen-containing organic compound, which includes a reaction tank for holding a liquid including the halogen-containing organic compound, an ultraviolet irradiation device for irradiating ultraviolet rays to the liquid, and an alkali addition device for adding an alkali to the liquid in the reaction tank. The reaction tank is formed into a hollow column shape including a hollow portion partitioned by an ultraviolet-transmissive inner peripheral wall, and the ultraviolet irradiation device is placed inside the hollow portion.

[Effect]

The apparatus is downsized and failures and the like of the apparatus can be reduced. Accordingly, the apparatus is excellent in light of handling and maintenance.



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(72) Inventor: Terinobu Hayata
8 shinnsugitamachi,Isogo-ku,Yokohama-shi, Kanagawa
c/o Kabushikikaisya Toshiba, Yokohama Jigyosyo

[Claims]
[Claim 1]

A decomposition apparatus for a halogen-containing organic compound for irradiating ultraviolet rays and thereby decomposing a halogen-containing organic compound, the decomposition apparatus being characterized by comprising:

a reaction tank for holding a liquid including the halogen-containing organic compound;

an ultraviolet irradiation device for irradiating ultraviolet rays to the liquid; and

an alkali addition device for adding an alkali to the liquid in the reaction tank,

wherein the reaction tank is formed into a hollow column shape including a hollow portion partitioned by an ultraviolet-transmissive inner peripheral wall, and

the ultraviolet irradiation device is placed inside the hollow portion.

[Detailed Description of the Invention]
[0001]
[Industrial field of the Invention]

The present invention relates to apparatuses for decomposing halogen-containing organic compounds, more specifically, to a decomposition apparatus configured to perform a decomposition reaction of a halogen-containing organic compound by means of ultraviolet irradiation.

[0002]
[Prior Art]

Halogen-containing organic compounds such as trichlene, polychlorobiphenyl (PCB) or chlorofluorocarbon are widely used in various fields such as chemical industries. However, toxicity to the human body becomes apparent in terms of chlorine compounds such as trichlene or PCB, and fluorine compounds such as chlorofluorocarbon causes a problem of destruction of the global environment. As described above, problems are coming out in recent years. Given this circumstance, methods of decomposing

and detoxifying halogen-containing organic compounds have been anticipated and various methods have been studied. One of the methods is an ultraviolet decomposition method.

[0003] In the ultraviolet decomposition method, ultraviolet rays are irradiated to a halogen-containing organic compound in a gas phase. However, decomposition efficiency is low because a decomposition reaction progress is hampered by a product generated in the course of the decomposition. In addition, there is also a higher risk as compared to other methods that the apparatus is damaged by corrosive halogen compound gas generated by the decomposition. Additionally, the method also tends to require a large-sized apparatus. For this reason, a liquid-phase irradiation method is proposed as an improvement in the ultraviolet decomposition method. In this method, a halogen-containing organic compound is introduced to a liquid medium, and after irradiating ultraviolet rays thereto, an alkali is added to remove and salt out hydrogen halide and the like.

[0004]

[Problems to be Solved by the Invention]

However, when performing the above-described liquid-phase irradiation method, it is necessary to carry out the ultraviolet irradiation and the alkali addition in different tanks in order to prevent deposited salt from being attached around an ultraviolet lamp. Therefore, the apparatus must include two or more tanks, and it is difficult to downsize the apparatus. Moreover, means for transferring the liquid medium between the two tanks is also required. Accordingly, the apparatus has a disadvantage in terms of cleaning the apparatus and maintenance thereof.

[0005]

[Means for Solving the Problems]

The present invention relates to an improvement in an apparatus for carrying out the above-described liquid-phase irradiation method. An object thereof is to provide a decomposition apparatus for a halogen-containing organic compound which can achieve downsizing, easy maintenance, and

the like.

[0006] A decomposition apparatus for a halogen-containing organic compound according to the present invention is a decomposition apparatus for a halogen-containing organic compound for irradiating ultraviolet rays and thereby decomposing a halogen-containing organic compound, which includes a reaction tank for holding a liquid including the halogen-containing organic compound, an ultraviolet irradiation device for irradiating ultraviolet rays to the liquid, and an alkali addition device for adding an alkali to the liquid in the reaction tank. Here, the reaction tank is formed into a hollow column shape including a hollow portion partitioned by an ultraviolet-transmissive inner peripheral wall, and the ultraviolet irradiation device is placed inside the hollow portion.

[0007]

[Operation]

The ultraviolet irradiation device irradiates ultraviolet rays to the liquid in the reaction tank through the ultraviolet-transmissive inner peripheral wall, and the decomposition of the halogen-containing organic compound thereby progresses. The ultraviolet irradiation device which is placed inside the hollow portion is isolated from the liquid in the reaction tank by the ultraviolet-transmissive inner peripheral wall, whereby a deposit generated by addition of the alkali to the liquid in the reaction tank after the irradiation of ultraviolet rays is prevented from being attached to the ultraviolet irradiation device.

[0008] Hereafter, the present invention will be described in detail.

[0009] In the liquid-phase irradiation method, the liquid including the halogen-containing organic compound is put into the reaction tank, then ultraviolet rays are irradiated while inserting an ultraviolet lamp into a central part of the liquid, and then the alkali is added so as to neutralize and salt out hydrogen halide which is generated in the liquid. When the salt is deposited while inserting the ultraviolet lamp, the salt is attached to the surface of the ultraviolet lamp. Accordingly, it is necessary

either to take the ultraviolet lamp out of the tank for cleaning, or to insulate the ultraviolet lamp from the liquid. Meanwhile, when cleaning the ultraviolet lamp, there is a possibility that a trouble causes a failure of the lamp due to the deposit. Therefore, to configure the ultraviolet irradiation device which is resistant to failures and the like and is capable of being downsized, it is important to eliminate the attachment of the deposit to the ultraviolet lamp.

[0010] In the present invention, the above-mentioned configuration is achieved by forming the shape of the reaction tank of the decomposition apparatus into a hollow column shape. Specifically, the reaction tank includes the hollow portion which is substantially partitioned by the ultraviolet-transmissive inner peripheral wall in the central part, while the ultraviolet lamp is inserted into the hollow portion and the liquid subject to the irradiation of ultraviolet rays is contained in the annular tank. Therefore, the ultraviolet lamp is isolated from the liquid subject to the irradiation of ultraviolet rays by the inner peripheral wall and the ultraviolet rays are irradiated to the liquid while passing through the inner side wall. The inner periphery and the outer periphery of the above-described reaction tank shaped like a hollow column may be formed into any shape including a circular column and a polygonal column. Moreover, it is not always necessary to form the reaction tank strictly into the column, and a barrel shape is also acceptable. However, it is preferable that the inner periphery and the outer periphery are formed into the circular column shapes in light of irradiation efficiency of the ultraviolet rays.

[0011] When using the above-described reaction tank, it is not possible to stir the liquid by disposing a usual stirring wing or the like in the center of the reaction tank. However, to enhance reaction efficiency, it is preferable to stir the liquid so as to render the reaction liquid always homogeneous. This is quite an important factor especially in case of a large-sized reaction tank. As a method suitable for solving this point, it is possible to cite a

bubbling method which is configured to provide a bubbling device on a bottom part of the reaction tank and to homogenize the reaction liquid by use of bubbles.

[0012] Fig. 1 is a graph showing a result of variations with time of decomposition ratios in ultraviolet decomposition of chlorofluorocarbon 12 observed by gas chromatograph concerning the bubbling method and the stirring method respectively by use of a usual cylindrical reaction tank. In the bubbling method, the ultraviolet irradiation is performed on isopropanol including chlorofluorocarbon 12 as the halogen-containing organic compound while bubbling air by use of a filter having pore diameters of 40 μm (bubble diameters: about 50 to 1000 μm). In the stirring method, the ultraviolet irradiation is performed on isopropanol including chlorofluorocarbon 12 while stirring by use of a magnetic core. An initial concentration of chlorofluorocarbon 12 was set to 3% in terms of a volume ratio, the ultraviolet lamp used therein had a dominant wavelength of 254 nm, and the irradiation was performed for 40 minutes. The decomposition ratios were obtained by calculating (the chlorofluorocarbon concentration before irradiation – the chlorofluorocarbon concentration at the time of measurement) × 100 / (the chlorofluorocarbon concentration before irradiation).

[0013] From Fig. 1, it is evident that the decomposition reaction can progress at high efficiency by the bubbling method. Therefore, it is possible to homogenize the reaction liquid sufficiently by fitting the bubbling device to the above-described reaction tank shaped like a hollow column and by bubbling. Concerning the bubbling device, it is needless to say that a gas introduction tube having numerous pores, a filter, and the like can be used as appropriate, and that normally implemented modifications concerning the shape and arrangement of the bubbling device are also feasible when necessary.

[0014] Various types of alcohol can be used as the liquid medium in the liquid-phase irradiation method. In particular, isopropanol is preferred in light of reactivity in ultraviolet decomposition.

Since the solubility of the halogen-containing organic compound to such an alcohol-based medium is generally high, it is possible to introduce a gaseous halogen-containing organic compound to the liquid medium easily and efficiently by bubbling. That is, the above-described bubbling method is not only capable of just homogenizing the reaction liquid but is also applicable as a method of introducing a highly volatile halogen-containing organic compound such as chlorofluorocarbon to a liquid phase for ultraviolet irradiation. When handling the volatile halogen-containing organic compound in a liquid state, losses due to gasification in the course of operations and environmental pollution become problematic. Accordingly, introduction of the halogen-containing organic compound to the liquid phase by bubbling is an effective method. By using the bubbling method, it is possible to introduce the halogen-containing organic compound which has been once gasified to the liquid phase for the ultraviolet irradiation, and a device for reliquefying the halogen-containing compound is not necessary.

[0015]

[Embodiments]

Embodiments of a decomposition apparatus introducing the above-described bubbling system in the reaction tank shaped like a hollow column will be described below.

[0016] Fig. 2 shows one embodiment of a decomposition apparatus according to the present invention. A decomposition apparatus 1 is an apparatus suitable for introducing a gaseous halogen-containing organic compound such as chlorofluorocarbon to a liquid phase by bubbling and for performing ultraviolet decomposition. The decomposition apparatus 1 includes an airtight reaction tank shaped like a hollow cylinder made of fused silica, and an ultraviolet lamp 5 installed in a standing manner at a cylindrical hollow portion in the center of the reaction tank 3. The ultraviolet lamp 5 is connected to a stabilized power supply 7. Below the hollow portion of the reaction tank 3, a fan 9 for air-cooling the ultraviolet lamp 5 is fitted, which sends air to the

hollow portion. The air supplied by the fan 9 passes through clearance between the lamp 5 and an inner peripheral wall of the reaction tank 3 and is discharged upward. Inside the reaction tank 3, a ring-shaped gas introduction tube 11 is annexed to a bottom part, and the introduction tube 11 is connected to a change cock 13 by a pipe penetrating an outer peripheral wall of the reaction tank 3. In addition, there is a gas outlet 15 in an upper part of the reaction tank 3, and a circulation path 17 for connecting the change cock 13 to the gas outlet 15 is provided. A pump 19 is disposed in the middle of the circulation path 17, so as to circulate gas through the reaction tank 3. The gaseous halogen-containing organic compound at normal temperature and normal pressure is supplied to the reaction tank 3 through the change cock 13. The change cock 13 has a function of monitoring pressure inside the reaction tank 3 and of controlling supply of the halogen-containing organic compound so as to maintain the pressure constant. Further, the reaction tank 3 is provided with a measuring machine for measuring the concentration of the halogen-containing organic compound in the liquid phase and a pH value thereof.

[0017] There is a solvent inlet 21 in the upper part of the reaction tank 3, and a solvent 25 is supplied from a solvent tank 23 through a pipe 27 and a pump 29. In this embodiment, isopropanol (hereinafter abbreviated as IPA) is used as the solvent. Moreover, an alkali inlet 31 is provided on the top of the reaction tank 3, and an alkali 35 is introduced from an alkali tank 33. In this embodiment, sodium alcoholate powder is used as the alkali.

[0018] In addition, a ring-shaped cleaning tube 37 having numerous holes is disposed on the upper part of the reaction tank 3. A cleaning liquid 39 is supplied from a cleaning water tank 41 to the reaction tank 3 through a cock 43 and the cleaning tube 37, whereby the inside of the container 3 is showered and cleaned. In this embodiment, a NaCl aqueous solution is used as the cleaning liquid.

[0019] Meanwhile, an outlet 45 is provided on the bottom part of

the reaction tank 3 and is connected to a liquid tank 23 and to a waste liquid tank 51 through pipes 47 and 49. Connection of the outlet 45 to the solvent tank 23 or the waste liquid tank 51 is changed by a cock 53. A sensor 55 is provided between the outlet 45 and the cock 53, and transmissivity of the liquid passing through the pipe 47 is monitored. The cock 53 is changed based on information concerning the transmissivity detected by the sensor 55.

[0020] A process of decomposing chlorofluorocarbon R12 as the halogen-containing organic compound by use of the above-described decomposition apparatus 1 will be shown below. Operations are carried out in accordance with a flowchart shown in Fig. 3.

[0021] Firstly, the IPA is supplied from the liquid tank 23 to the reaction tank 3 by the pump 29 so as to pool a predetermined amount of IPA in the reaction tank 3 (Step 57). Next, ultraviolet irradiation is started (Step 59), and a predetermined amount of chlorofluorocarbon is injected from the gas introduction pipe 11 into the IPA (Step 65). Then bubbling is started while changing the cock 13 (Step 67). The chlorofluorocarbon which cannot be dissolved in the IPA at a time is discharged to the gas phase in the container 3. However, such chlorofluorocarbon is circulated by the pump 19 during the bubbling and is introduced to the IPA again. The chlorofluorocarbon concentration is detected while performing the bubbling for a predetermined period of time (Steps 61 to 69). The chlorofluorocarbon is added when the chlorofluorocarbon concentration in the liquid phase falls below a predetermined amount (Step 61), and gas phase pressure is detected so that the gas phase pressure is maintained to be equal to or above predetermined pressure (Step 63). The chlorofluorocarbon R12 in the IPA undergoes the ultraviolet decomposition efficiently by a solvation effect, and is decomposed into a primary decomposition product R22 in which one of chlorine atoms is substituted by hydrogen.

[0022] After passage of a predetermined period of time, the

bubbling and the ultraviolet irradiation are stopped (Steps 71 and 73) and the alkali is added (Step 75). By addition of the alkali, the primary decomposition product R22 is further converted into a secondary decomposition product R32, in which another chlorine atom is substituted by hydrogen, and into methane. Simultaneously, hydrogen halide generated by the decomposition is neutralized and salted out, and part of such salt may be attached to the inner wall of the reaction tank 3. Thereafter, the NaCl aqueous solution in the cleaning water tank 41 is supplied from the cleaning tube 37 (Step 77). At this time, the IPA is separated from water containing an electrolyte and the excessive alkali in the IPA is dissolved in the NaCl aqueous solution. The pH value of the IPA phase is measured and the addition of the NaCl aqueous solution is repeated until the excessive alkali transfers to the water phase almost completely (Steps 77 and 79).

[0023] Thereafter, the cock 53 is controlled such that the reaction tank 3 and the waste liquid tank 51 communicate with each other, and the liquid in the reaction tank 3 is discharged from the outlet 45 (Step 81). Then, the sensor 55 is activated (Step 83). The sensor 55 monitors the transmissivity of the discharged liquid (Step 85), and after detecting the discharged liquid changing from the aqueous solution to the IPA in accordance with the change in the transmissivity, the sensor 55 controls the cock 53 and thereby guides the discharged liquid to the solvent tank 23 (Step 87). When the solvent in the reaction tank 3 is fully discharged, the cock 53 is again changed to the waste liquid tank 51 and the NaCl aqueous solution is supplied from the cleaning tube 37, and the salt and the like attached to the inner wall of the reaction tank 3 is washed away (Step 89).

[0024] The IPA collected by the above-described operations contains a very small amount of acetone which is a side reaction product. However, acetone functions as a photosensitizer in an ultraviolet decomposition reaction in a state without an alkali. Accordingly, the collected IPA can be effectively recycled by repeating the above-described operations.

[0025] In the above-described operations, separation of the solvent and the generated salt is carried out according to liquid-liquid separation utilizing the property that the IPA is separated from the water containing the electrolyte. However, when using a hydrophilic solvent other than the IPA as the liquid medium, it is possible to carry out solid-liquid separation of the solvent and the deposited salt without adding the cleaning water. In light of irradiation efficiency of the ultraviolet rays, it is preferable to cover the outer periphery of the above-described reaction tank 3 with a film or the like which reflects ultraviolet rays. Alternatively, it is also possible to fabricate only the inner peripheral wall of the reaction tank 3 by use of an ultraviolet-transmissive material and to form other parts by use of an ultraviolet-shielding material.

[0026] Here, as described in Fig. 1, application of the bubbling method is effective for promoting the decomposition reaction and is also suitable for dealing with continuous operations. Accordingly, it is also possible to achieve downsizing of the decomposition apparatus and to improve processing capacity by configuring the decomposition apparatus as shown in Fig. 4. This apparatus applies an ultraviolet lamp 5 including a normal cooling tube 5a without using the reaction tank shaped like a hollow column, and configures the reaction tank separately by use of an ultraviolet irradiation tank 3a and an alkali addition tank 3b. However, by utilizing the promotion of the decomposition reaction owing to the bubbling caused by a gas introduction tube 11a at the bottom of the irradiation tank 3a, it is possible to downsize the irradiation tank 3a and the alkali addition tank 3b by circulating the solvent through the irradiation tank 3a, the alkali addition tank 3b, and the solvent tank 23 in a relatively short cycle. This apparatus performs the ultraviolet decomposition operation and the alkali addition and separation operations in parallel at the same time, and therefore exerts effectiveness particularly when repeating decomposition processing of a halogen-containing compound.

[0027]

[Effect of the Invention]

As described above, according to the present invention, the decomposition apparatus for a halogen-containing organic compound is downsized, and failures and the like of the apparatus can be reduced. Accordingly, the apparatus is excellent in light of handling and maintenance, and an industrial value thereof is significant.

[Brief Description of the Drawings]

[Figure 1]

Fig. 1 is a graph showing variations with time of decomposition ratios of chlorofluorocarbon 12 when performing ultraviolet irradiation in accordance with a stirring method and a bubbling method.

[Figure 2]

Fig. 2 is a schematic diagram showing one example of a decomposition apparatus for a halogen-containing organic compound of the present invention.

[Figure 3]

Fig. 3 is a flowchart showing an operation example of the decomposition apparatus shown in Fig. 2.

[Figure 4]

Fig. 4 is a schematic diagram showing another exapmle of the decomposition apparatus for a halogen-containing organic compound of the present invention.

[Explanation of referenced numerals]

3 REACTION TANK
5 ULTRAVIOLET LAMP
11, 11a GAS INTRODUCTION TUBES
23 SOLVENT TANK
33 ALKALI TANK
41 CLEANING WATER TANK
51 WASTE LIQUID TANK

Fig. 1

CHLOROFLUOROCARBON DECOMPOSITION RATIO (%)

IRRADIATION TIME (MIN.)

a: BUBBLING

b: MAGNETIC STIRRING

Fig. 3

START

57 POOL IPS

59 START UV IRRADIATION

61 PREDETERMINED CHLOROFLUOROCARBON CONCENTRATION?

63 PREDETERMINED PRESSURE?

65 INJECT CHLOROFLUOROCARBON

67 START BUBBLING

69 PREDETERMINED TIME ELAPSED?

71 STOP BUBBLING

73 STOP UV IRRADIATION

75 ADD ALKALI

77 CLEAN WITH NaCl AQUEOUS SOLUTION

79 IPA PHASE pH= 7?

81 DISCHARGE TO WASTE LIQUID TANK

83 ACTIVATE SENSOR

85 TRANSMISSIVITY (IR= 300 nm) T=50%?

87 DISCHARGE TO SOLVENT TANK

89 CLEAN REACTION TANK WITH NaCl AQUEOUS SOLUTION

91 DISCHARGE CLEANING WATER

END

Fig. 1

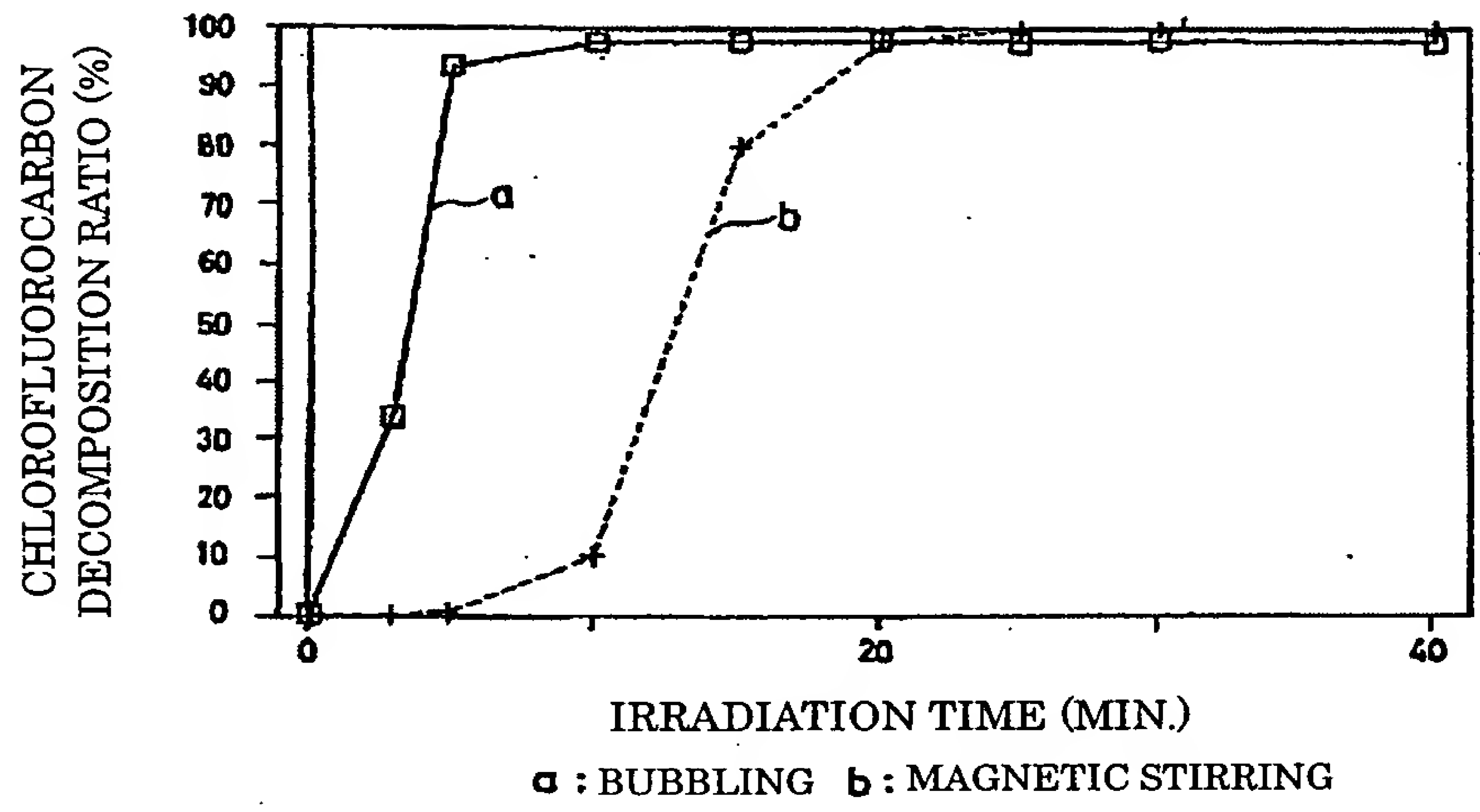
CHLOROFLUOROCARBON DECOMPOSITION RATIO (%)
100
90
80
70
60
50
40
30
20
10
0
a
b
0
20
40
IRRADIATION TIME (MIN.)
a : BUBBLING b : MAGNETIC STIRRING

Fig. 2

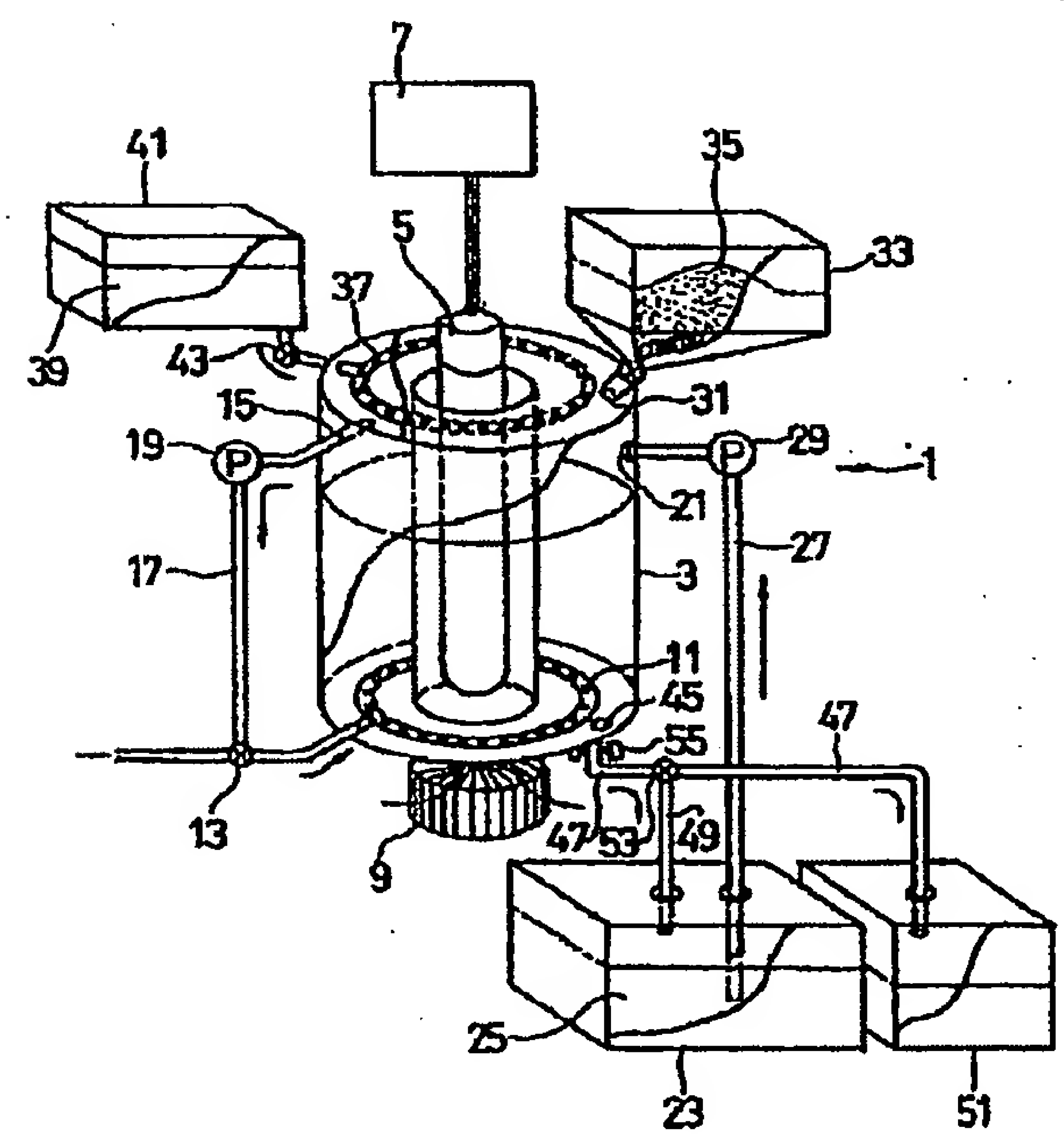
7
41
35
5
33
37
39
43
15
31
19
P
P
29
1
21
17
27
3
11
45
55
47
13
47
53
49
9
25
23
51

Fig. 3

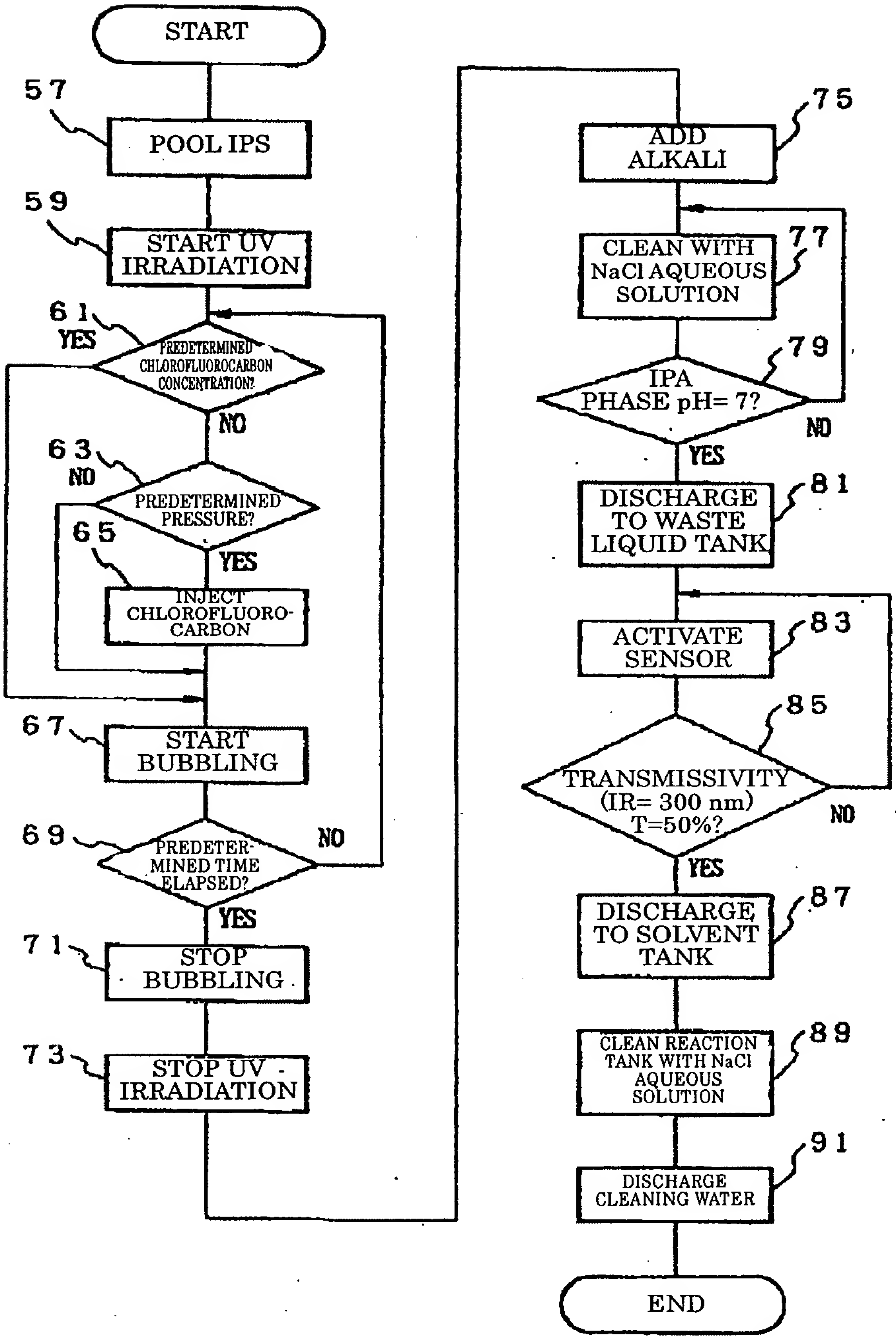
START
57
POOL IPS
59
START UV IRRADIATION
61
YES
PREDETERMINED CHLOROFLUOROCARBON CONCENTRATION?
NO
63
NO
PREDETERMINED PRESSURE?
YES
65
INJECT CHLOROFLUORO-CARBON
67
START BUBBLING
69
PREDETER-MINED TIME ELAPSED?
NO
YES
71
STOP BUBBLING
73
STOP UV IRRADIATION
75
ADD ALKALI
77
CLEAN WITH NaCl AQUEOUS SOLUTION
79
IPA PHASE pH= 7?
NO
YES
81
DISCHARGE TO WASTE LIQUID TANK
83
ACTIVATE SENSOR
85
TRANSMISSIVITY (IR= 300 nm) T=50%?
NO
YES
87
DISCHARGE TO SOLVENT TANK
89
CLEAN REACTION TANK WITH NaCl AQUEOUS SOLUTION
91
DISCHARGE CLEANING WATER
END

Fig. 4